Vibrational degrees of freedom in the Total Collision Energy DSMC chemistry model

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Abstract

The Total Collision Energy (TCE) model is used to simulate chemical reactions in the Direct Simulation Monte Carlo method. Colliding particle pairs with total collision energy (translational plus internal energy) greater than an activation energy are accepted for reaction with a probability which depends on the amount of the collision energy in excess of the activation energy. Constants in the probability function are adjusted to match experimentally determined rates in an Arrhenius form under thermal equilibrium conditions. The model thus attempts to extrapolate equilibrium reaction rates to non-equilibrium conditions by using microscopic based information from colliding particle pairs. However, the number of active 'degrees of freedom' (DOF) in the vibrational energy mode contributing to the total collision energy must be specified for each collision pair; various methods have been proposed for this. It is shown that the different calculation methods can alter the equilibrium reaction rate returned by the TCE model, and can have significant effects throughout non-equilibrium flowfields. If we assume, as is usual, that all of the internal energy is available for the reaction, we consider that the most consistent and physically intuitive approach is to determine the number of active DOF from the local macroscopic temperatures in the cell.

1 Introduction

In the Total Collision Energy (TCE) DSMC chemistry model [1] not all particle pairs with a collision energy E_c greater than a reaction activation energy E_a undergo a chemical reaction; a reaction probability function P is specified which depends on the excess energy $\Delta E = E_c - E_a$. Some decisions must be made about how much of the structure energy of the colliding molecules (usually the rotational and vibrational energy) is available for redistribution to other modes during the collision. In most applications of interest, we may assume a continuous distribution of rotational energy with the classical integer number ζ_r of degrees of freedom (DOF). However, quantum vibrational energy levels are spaced at much larger intervals than for rotational energy. The continuous distribution may be used as an approximation if a parameter ζ_v representing the 'effective number' of active DOF is supplied.

The reaction probability P for a colliding pair depends on the total mean effective number of degrees of freedom $\bar{\zeta} = \zeta_r + \bar{\zeta}_v$ for all possible collision pairs. The form of P has been chosen [1] such that, when the molecular velocities of colliding molecules conform to the Maxwell-Boltzmann distribution, the rate at which chemical reacting collisions occur corresponds to a reaction rate coefficient in a modified Arrhenius form

$$k_f = A\,(T/\theta_d)^{\eta} \exp\left(-\theta_d/T\right) \tag{1}$$

where $\theta_d \equiv E_a/k$, is the 'dissociation temperature', k is Boltzmann's constant and A is a constant with units of m^3/s. For the desired equilibrium chemical rates to be reproduced, $\bar{\zeta}$ must be chosen to match the actual number of degrees of freedom which contributes toward the reaction energy. If $\bar{\zeta}$ does not match the value corresponding to the actual distribution of energy available for the reaction, then the expected equilibrium reaction rate will not be returned. In addition, since $\bar{\zeta}$ defines the functional form of $P(E_c)$, it can have a marked effect on the reaction rate in conditions of the thermal non-equilibrium.

At least three methods of determining $\bar{\zeta}_v$ in each collision have been used. For a given vibrational mode, all of the methods predict a value of $\bar{\zeta}_v$ for diatomic molecules between zero (no excitation) and two (fully excited). The three methods are:

1. A constant value of $\bar{\zeta}_v$ may be used throughout the flow, for all collisions. If the temperature is sufficiently high, $\bar{\zeta}_v$ can be set to the classical (fully excited) value. Alternatively a smaller constant value of $\bar{\zeta}_v$ (partial excitation) can be specified; this is equivalent to assuming that the entire flow can be described by a single characteristic temperature. The first method has been used by Boyd [2] and the second by Haas [3].

2. The value of $\bar{\zeta}_v$ may be assumed constant for all collisions in any one cell for each time step, although it may vary from cell to cell and as the simulation progresses. The constant value for the cell can be evaluated as the value appropriate to the local macroscopic conditions. Estimates of these local conditions are known in a typical DSMC calculation and it is a simple matter to calculate an appropriate value of $\bar{\zeta}_v$ for each cell. This 'macroscopic method' has been used by Gimelshein *et al.* [4] and Lilley and Macrossan [5, 6, 7].

3. As proposed by Boyd [2], a new value of $\bar{\zeta}_v$ can be evaluated for each collision, based on an effective 'collision temperature' for each collision. Two gamma functions (the 'constant' C_1 in Eq. 4) must be evaluated for every collision.

Gimelshein *et al.* [4] have previously investigated the error in equilibrium reaction rate introduced by approximating the quantized distribution of vibrational energy as a continuous distribution. They show that these discrepancies exist even when the value of $\bar{\zeta}_v$ is evaluated using the local vibrational temperature (*i.e.* method 2). Here we investigate the additional effect of using a value of $\bar{\zeta}_v$ which does not match that evaluated using the local vibrational temperature. In particular, we examine the influence of a 'collision' computed value and two characteristic flow-field values of $\bar{\zeta}_v$. We consider the simple dissociation reaction for pure diatomic oxygen.

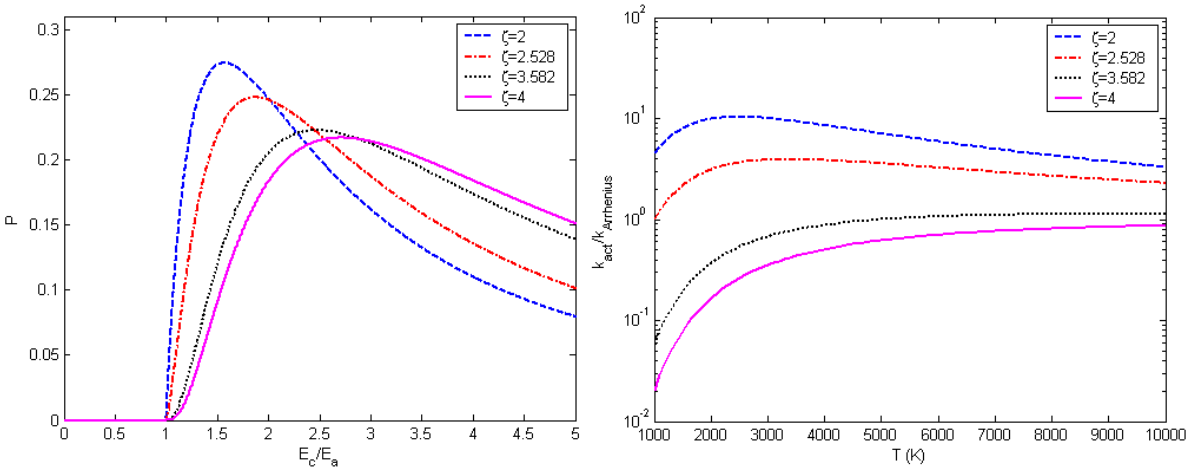

Figure 1: Left: Variation of O_2–O_2 dissociation probability P (Eq. 3) versus E_c for four different numbers of vibrational degrees of freedom. Right: Ratio of equilibrium reaction rate to Arrhenius reaction rate as a function of temperature for four values of $\bar{\zeta}$ in Eq. 3

2 The TCE reaction probability function

The TCE model applies to variable hard sphere (VHS) molecules for which the total collision cross-section σ as a function of the relative collision speed g is given by

$$\sigma = \sigma_{\text{ref}} \left(g_{\text{ref}}/g\right)^{2\nu}. \tag{2}$$

The probability P that a given collision pair with collision energy $E_c > E_a$ will undergo a reaction is given by

$$P = C_1 \left(\frac{A}{g_{\text{ref}}\sigma_{\text{ref}}}\right) \left(1 - \frac{E_a}{E_c}\right)^{1-\nu+\bar{\zeta}} \left(\frac{E_c}{E_a} - 1\right)^{\eta+\nu-\frac{1}{2}}. \tag{3}$$

Here the 'constant' C_1 depends on the value of $\bar{\zeta}$ and is given by

$$C_1 = S\pi^{\frac{1}{2}} \left(\frac{T_{\text{ref}}}{\theta_a}\right)^{\frac{1}{2}-\nu} \frac{1}{2\Gamma(2-\nu)} \frac{\Gamma(2-\nu+\bar{\zeta})}{\Gamma\left(\frac{3}{2}+\eta+\bar{\zeta}\right)}. \tag{4}$$

where $S = 1$ or $\frac{1}{2}$ is a symmetry factor, $T_{\text{ref}} = \widetilde{m} g_{\text{ref}}^2/(2k)$ and $\widetilde{m}$ is the reduced mass. The rate coefficient at equilibrium is derived from P as $k_f = \int_{E_a}^{\infty} P\sigma g f dE_c$ where f is the equilibrium distribution function for total collision energy for VHS simulator particles. This rate coefficient will match the Arrenhius expression of Eq. 1 if the value of $\bar{\zeta}$ is equal to the mean value of ζ in the distributing of reacting collision pairs.

The variation of the probability function P for values of the ratio E_c/E_a between one and five is shown in the left plot of Figure 1 using the data in Eqs. 6 and 8 for $O_2 - O_2$ reactions. The figure shows P vs E_c/E_a for four values of $\bar{\zeta}$ ($\bar{\zeta} = 2, 2.528, 3.582, 4$) corresponding to $T_v = 0$ K, 1000 K, 5000 K and $T_v >> \theta_v$.

The overall reaction rate is largely determined by the shape of the probability function at low collision energies; there is a significant difference in the shape even at small values of E_c/E_a. The ratio of the predicted equilibrium to Arrhenius reaction rate as a function

of temperature for each of the assumed values of $\bar{\zeta}$ is shown in the right plot of Figure 1. A value of $\bar{\zeta}$ which does not match that in the actual energy distribution can result in an order of magnitude variation in the equilibrium reaction rate. Values of $\bar{\zeta}$ which are less than the corresponding number in the equilibrium distribution, result in a faster reaction rate at a given temperature.

It is important to note that, although the choice of the number of internal degrees of freedom contributing to the reaction energy influences the shape of P (and hence the non-equilibrium reaction rates), if the assumed value of $\bar{\zeta}$ matched the chosen number of degrees of freedom contributing to the reaction energy, then each of the above values of $\bar{\zeta}$ would result in the same equilibrium reaction rate. It is only the deviation between the assumed value of $\bar{\zeta}$ and the actual value which causes the difference in reaction rate (not withstanding the issue of quantized distributions discussed by Gimelshein *et al.* [4]). This difference in reaction rate may be an important consideration in typical aerospace applications.

3 Flowfield study

We have used the TCE model with the three strategies for setting $\bar{\zeta}_v$ to calculate the Mach 30 flow of molecular oxygen about a vertical flat plate, normal to the free-stream velocity. The free-stream is pure O_2, the velocity is $u_\infty = 9910$ m/s, the density $\rho_\infty = 10^{-6}$ kg/m^3 and the temperature $T_\infty = 300$ K. The ratio of a characteristic flow time to a characteristic reaction time (a Damkhöler number) evaluated at the conditions downstream of a normal shockwave in the free-stream is

$$D = \frac{L/u_s}{k_f\left(T_s\right) n_s} = 0.62. \tag{5}$$

Here n_s and u_s are the number density and velocity downstream of the shock, k_f is the dissociation rate evaluated just downstream of the shock and $L = 0.1$ m is the plate half-height. The value of D (close to one) indicates that a significant number of chemical reactions can be expected to occur in the vicinity of the plate. In this study, three body recombination reactions can be ignored due to the very low density.

The following reaction rates of Park [8] were used:

$$\begin{array}{rcll} O_2 - O_2 & : & k_f = 2.288 \times 10^{-16}\left(T/\theta_d\right)^{-1.5} \exp\left(-\theta_d/T\right) & \mathrm{m}^3/\mathrm{s} \\ O_2 - O & : & k_f = 1.144 \times 10^{-16}\left(T/\theta_d\right)^{-1.5} \exp\left(-\theta_d/T\right) & \mathrm{m}^3/\mathrm{s}. \end{array} \tag{6}$$

The Chapman-Enskog viscosity of VHS molecules, for which the scattering is isotropic and the total cross-section is given by Eq. 2, is $\mu = \mu_{\mathrm{ref}}\left(T/T_{\mathrm{ref}}\right)^{\nu+1/2}$ where

$$\mu_{\mathrm{ref}} = \frac{15\pi^{1/2}}{8\Gamma\left(4-\nu\right)} \frac{\widetilde{m} g_{\mathrm{ref}}}{\sigma_{\mathrm{ref}}}, \tag{7}$$

and where $g_{\mathrm{ref}} = \sqrt{2kT_{\mathrm{ref}}/\widetilde{m}}$. The following parameters at a reference temperature T_{ref} =1000 K were used:

$$\begin{array}{rcll} O_2 - O_2 & : & \mu_{\mathrm{ref}} = 4.91 \times 10^{-5}\mathrm{Ns/m}^2, & \nu = 0.19 \\ O_2 - O & : & \mu_{\mathrm{ref}} = 4.50 \times 10^{-5}\mathrm{Ns/m}^2, & \nu = 0.25 \\ O - O & : & \mu_{\mathrm{ref}} = 4.70 \times 10^{-5}\mathrm{Ns/m}^2, & \nu = 0.28. \end{array} \tag{8}$$

The nominal freestream mean free path, $\lambda_\infty = 2\mu_\infty/\rho_\infty \bar{c}$, is equal to the plate half-height. Here $\bar{c} = \sqrt{8kT_\infty/(\pi m)}$ is the free-stream mean thermal speed. The flow is two-dimensional with a plane of symmetry parallel to the freestream velocity. Half the flow-field is computed. The plate is diffusely reflecting, with a temperature of 300 K; complete accommodation in the rotational mode and no accommodation in the vibrational mode are assumed. A serial application [9] of the Borgnakke-Larsen procedure is used for internal energy relaxation with constant relaxation probabilities of 0.2 and 0.02 for the rotational and vibration modes respectively. The TCE chemistry model and VHS collision model were implemented following Bird [9]. The proportional energy exchange model of Hass [3] was used to distribute the post-collision internal energy amongst the various modes. The characteristic vibrational temperature of oxygen was taken as θ_v =2256 K.

DSMC results are presented for different chemical collision procedures:

1. Constant values of $\zeta_v = 0.528$ and $\zeta_v = 1.582$ corresponding to $T_v = 1000$ K and $T_v = 5000$ K in Eq. 9.

2. The time-averaged local vibrational temperature was used to derive ζ_v for each cell using an unbound simple harmonic oscillator vibrational model. Thus:

$$\zeta_v = \frac{2\theta_v/T_v}{\exp(\theta_v/T_v) - 1} \tag{9}$$

3. The relative translational collision temperature of each particle pair was calculated from the collision relative velocity g as

$$T_c = \frac{\widetilde{m} g^2}{(4 - 2\nu)\, k}. \tag{10}$$

   Eq. 9 with $T_v = T_c$ is then used to derive ζ_v for each collision.

Translational temperature and atomic oxygen mole fraction profiles along the stagnation streamline are shown in Figures 2 and Figure 3. The peak translational temperature is significantly different between the cases. Running from the highest temperatures, the cases lie in the order $\zeta_v(T_c)$, $\zeta_v\,(5000)$, $\zeta_v\,(T_{\text{cell}})$, $\zeta_v\,(1000)$. The predicted peak translational temperatures within the shock lie within a range of approximately ± 1000 K. It can be seen from these plots that for this simulation, a higher number of vibrational degrees of freedom in the TCE probability function corresponds to a lower rate of chemical reactions. This is consistent with the trends previously observed in the reaction rates (see Fig 1). The atomic oxygen mole fractions in front of the plate lie within a range of approximately $\pm 4\%$. Downstream of the plate, this difference is maintained.

Coefficients of drag, shear and heat transfer for the vertical plate are shown in Table 1. The drag and shear coefficients are generally not sensitive to the details of the flow-field chemistry. There is a small difference in the heat transfer to the plate. These values are consistent with the previous results with the variable case located between the $\zeta_v\,(1000)$ and $\zeta_v\,(5000)$ cases.

Note that two gamma functions must be evaluated for each collision to find the value of the 'constant' C_1 in Eq. 3. When a constant value of $\bar{\zeta}$ is used (method 1) throughout the flow-field, C_1 need only be calculated once, at the beginning of the simulation, for

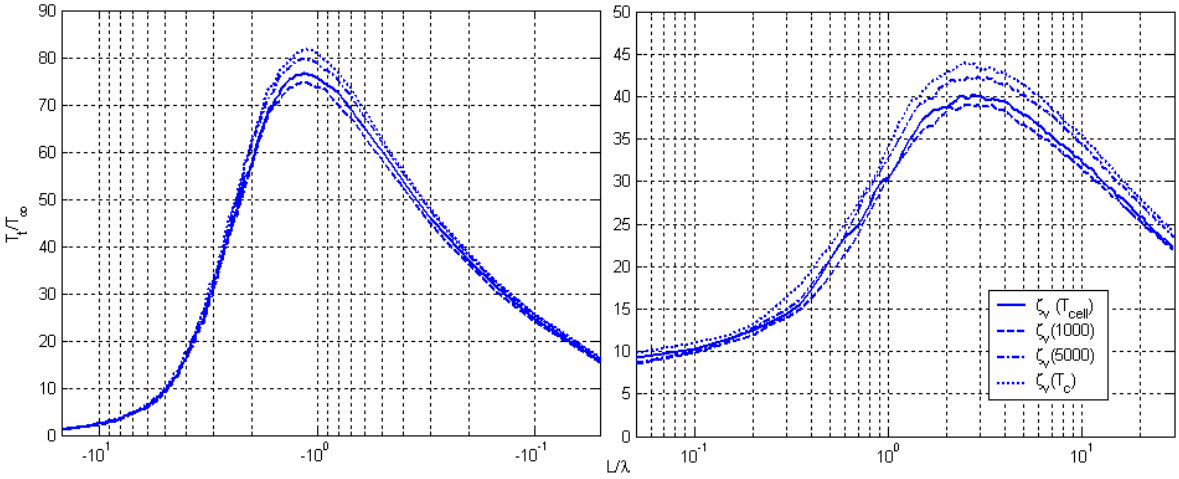

Figure 2: Translational temperature along the centre-line before (left) and after (right) the vertical plate. The temperature is normalized by the free-stream temperature and the distance by the upstream nominal mean free path $\lambda = 2\mu/(\rho\bar{c})$

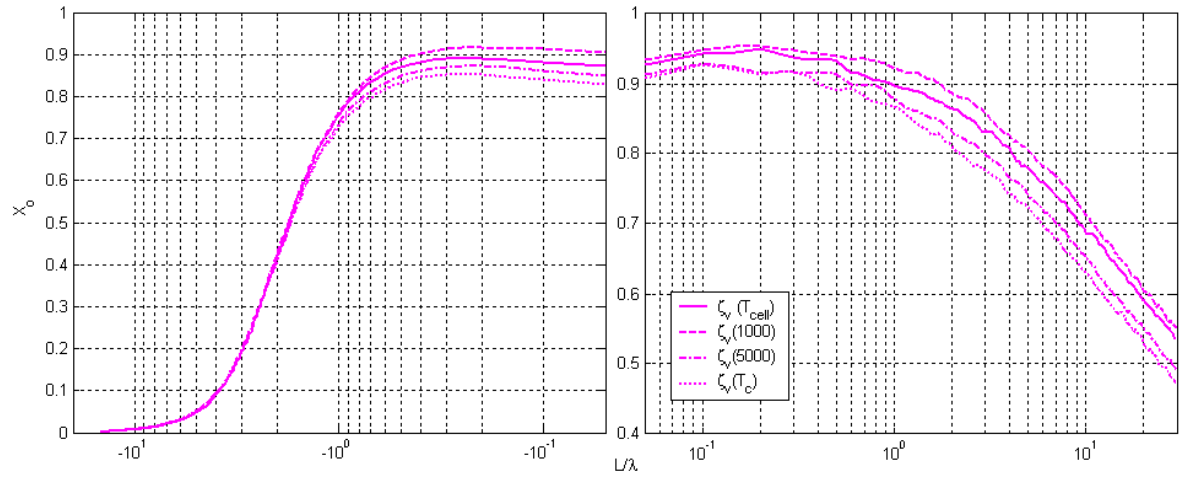

Figure 3: Atomic oxygen mole fraction along the centre-line before (left) and after (right) the vertical plate.The distance is normalized by the upstream nominal mean free path $\lambda = 2\mu/(\rho\bar{c})$.

Case	C_D	C_S	C_H	C_H normalized
$\zeta_v(T_{\text{cell}})$	1.951	0.118	0.454	1
$\zeta_v(T_c)$	1.953	0.118	0.469	1.03
$\zeta_v(1000)$	1.953	0.118	0.446	0.98
$\zeta_v(5000)$	1.957	0.119	0.463	1.02

Table 1: Drag, shear and heat transfer coefficients for the vertical plate.

collisions between particles of two specific species. For the macroscopic approach (method 2), C_1 is evaluated once for each cell only at each time step. When a collision temperature is employed (method 3), the two gamma functions must be computed at each potential reacting collision. Hence, it is apparent the most computationally efficient method is to use a constant value of $\bar{\zeta}$. The next most efficient is the cell-based temperature approach and the lest efficient is the collision temperature method.

The unbound reaction probability which exists when $E_c \rightarrow E_a$ for values of $\bar{\zeta}_{\text{int}} < -(\frac{1}{2} + \eta)$ was not encountered for this simulation since $\eta = -1.5$ and $\bar{\zeta} \geq 2$.

4 Conclusions

We have shown that the choice of a constant or variable number of vibrational DOF, and the temperature with which to evaluate the flow-field characteristic number for the constant case, can be important considerations. Although we have not compared the different flow-field results with experimental data, it is clear that the particular method chosen to evaluate $\bar{\zeta}$ can result in discrepancies between the equilibrium TCE and experimental reaction rates. For the flow-field conditions chosen, this lead to significant changes in the temperatures and mole-fractions predicted along the stagnation streamline.

In theory, a collision-based DSMC chemistry procedure should not require macroscopic information; the macroscopic information should be 'known' from the sampling of potential collision partners having velocities and internal energies representing the non-equilibrium distribution in the each cell. However, use of a collision pair calculated value of ζ_v, whilst appealing from a particle based standpoint, can nevertheless result in incorrect reaction rates at equilibrium since ζ_v is not calculated from the actual vibrational energy distribution. Gimelshein *et al.* [4] state this by noteing that it is not a good idea to use the collision energy dependent DOF because the constants in the probability function are determined *a priori* by integrating over collision energies and any energy dependence on the particle pair collision energy would alter the equilibrium reaction rate returned by the TCE model.

Since the number of vibrational degrees of freedom ζ_v varies with temperature, the 'constant' C_1 in Eqs. 3 and 4 should vary with temperature. This variation with temperature may be small in many applications, and it may be practical to use a single constant of ζ_v for the entire flow. Indeed it appears that for this case, if a constant characteristic vibrational temperature of approximately 2000 K were used to evaluate ζ_v, then the results would be similar to the variable 'macroscopic' case. Yet given the arbitrary nature of selecting the flow-field characteristic DOF beforehand, it makes sense to use the cell-based temperature to calculate the DOF, and hence to obtain the closest match to the desired equilibrium reaction rate, notwithstanding additional errors which are always present due to the quantized nature of the distribution.

In order for the correct equilibrium reaction rate to be reproduced at a given temperature, the assumed number of DOF in the TCE probability function must match the number contributing to the reaction energy. The obvious procedure is thus to use the local cell vibrational temperature to determine the number of vibrational degrees of freedom, and in comparison to the collision temperature approach, it is also more computationally efficient to do so.

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